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(57) Abstract

A thermally stable electrically conductive polyaniline comprising a polyaniline homopolymer or copolymer doped with an organic phosphorus acid.

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ELECTRICALLY CONDUCTIVE POLYANILINE WITH PHOSPHORUS-CONTAINING DOPANT

1. Field of the Invention

This invention relates to thermally stable electrically conductive substituted or unsubstituted polyanilines, and to compositions comprising such polyanilines and other electrically conductive or non-conductive materials such as polymers. Another aspect of this invention relates to a method of using such polyanilines and compositions to give conducting polymer articles, including films, parts, inks, adhesives, printings, fibers and coatings, and to a method for fabricating such articles.

2. Prior Art

There has recently been an increased interest in the electrochemistry and electrical phenomena of polymeric systems having extended conjugation in at least one backbone chain such as polyaniline. See for example, U.S. Patent No. 5,008,041, WO90/13601, EP Appl. 0399299A2 Cao et al., Polymer, 1989, vol. 30, pp. 2505-2311, U.S. Patent No. 4,983,322, 4,462,929, 3,963,498 and 4,025,463; European Patent No. 0017717; U.S. Patent Nos. 4,855,361, 4,798,685, 4,806,271, 4,822,638, 4,851,487, 4,798,685 and 5,069,820; and PCT WO90/10297.

SUMMARY OF THE INVENTION

One aspect of the present invention relates to a thermally stable, electrically conductive polyaniline comprised of a polyanilin homop lym r r cop lym r and

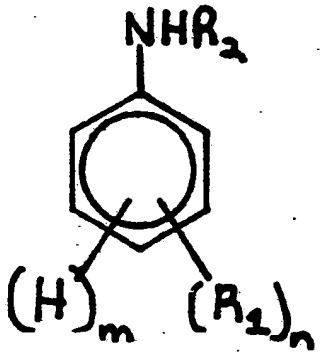
doped with an or more organic "thermally stable phosphorous acid dopant" and to articles fabricated from said polyaniline. As used herein a "phosphorus acid" is an organic acid which includes at least one protonic acid moieties and at least one phosphorus atoms.

This invention also relates to a composition comprising a polyaniline of this invention and one or more organic or inorganic materials as for example a composition comprising a matrix of one or more thermoplastic polymers, one or more thermosetting resins or a combination thereof having dispersed therein one or more doped polyanilines of this invention, and to articles formed from this composition and to a process for forming the compositions of this invention. This invention provides several unexpected benefits. For example, the electrically conductive polyaniline of this invention exhibits enhanced thermal stability.

DETAILED DESCRIPTION OF THE INVENTION

The thermally stable electrically conductive polyaniline of this invention comprises two essential ingredients. One essential ingredient is a substituted or unsubstituted polyaniline. As used herein, a "polyaniline" is a homopolymer or a copolymer in which at least 50 mole % of the recurring monomeric units are derived from unsubstituted or substituted anilines of the formula:

Formula I



wherein:

n is an integer from 0 to 5;

m is an integer from 0 to 5, with the proviso that the sum of n and m is equal to 5 and with the further proviso that at least one position on the aniline ring, preferably the para position, is substituted with a substitutent which will allow coupling of aniline rings such or halo, hydrogen or other leaving group, to form polyaniline;

R_1 is the same or different at each occurrence and is selected from the group consisting of phosphonic acid or salts or esters thereof, cyano, nitro, boric acid or salts or esters thereof, phosphoric acid or salts or esters thereof, halo, carboxylic acid or salts or esters thereof, phosphonic acid or salts or esters thereof, halo, hydroxy, cyano, sulfinic acid or salts or esters thereof, phosphinic acid and salts or esters thereof, amido, hydroxyamine, sulfonic acid and salts or esters thereof, nitro, deuterium, amino, or substituted or unsubstituted alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkyl, aryloxy, alkylthioalkyl, arylalkylamino, alkylaryl, arylalkyl, alkylamino, arylamino, dialkylamino, diarylamino, aryl, alkylsulfinyl, aryloxyalkyl, alkylsulfinylalkyl, alkoxyalkyl, alkylsulfonyl, arylthio, alkylsulfonylalkyl, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, alkylsilane or alkyl wherein permissible substituents are one or more phosphonic acid or salts or esters thereof, sulfonic acid or salts or esters thereof, phosphoric acid or salts or esters thereof, boric acid or salts or esters thereof, sulfate, sulfinic acid or salts or esters thereof, quaternary ammonium, hydroxylamine, amido, phosphinic acid or salts or esters thereof, carboxylic acid or salts or esters thereof, halo, nitro, cyano or epoxy substituents; or any two R_1 groups together or one or more R_1 groups together with an R_2 group may form a substituted or unsubstituted alkylene, alkenyl or alkynylene chain completing a 3, 4, 5, 6,

7, 8, 9 or 10 membered aromatic, heteroalicyclic, heter aromatic r alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur, sulfinyl, ester, carbonyl, sulfonyl, or oxygen atoms wherein permissible substituents are one or more phosphonic acid or a salt or an ester derivative, sulfonic acid or a salt or an ester derivative, phosphoric acid or a salt or an ester derivative, boric acid or a salt or an ester derivative, sulfate, sulfinic acid or a salt or an ester derivative, or a salt or an ester derivative thereof, quaternary ammonium, amido, hydroxylamine, phosphinic acid or a salt or ester thereof, carboxylic acid or a salt or ester thereof, hydroxyamino, halo, nitro, cyano or epoxy moieties; or R_1 is a divalent organic moiety bonded to the same or a different substituted or unsubstituted aniline moiety or R_1 is an aliphatic moiety having repeat units of the formula:

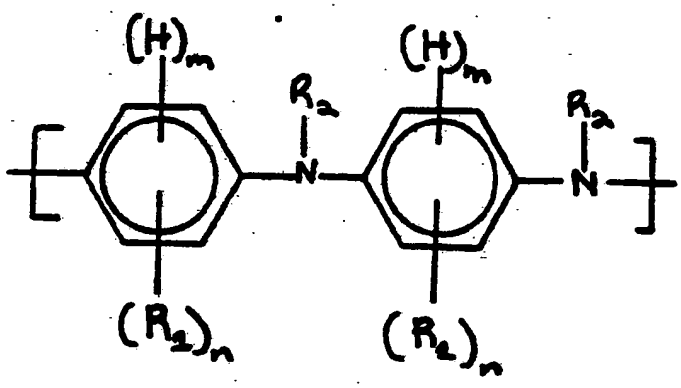
$$(OCH_2CH_2)_qO\text{-}CH_3,\ (OCH_2CH(CH_3))_qO\text{-}CH_3,$$
$$(CH_2)_q\ CF_3,\ (CF_2)_q\text{-}CF_3 \text{ or } (CH_2)_q\ CH_3$$

wherein q is a positive whole number; and

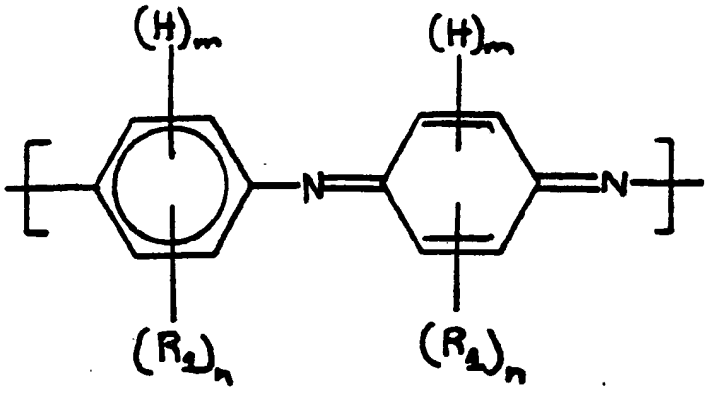
R_2 is the same or different at each occurrence and is hydrogen or R_1, preferably hydrogen.

Preferred polyaniline consists of repeat units of the Formulas II and/or III:

Formula II

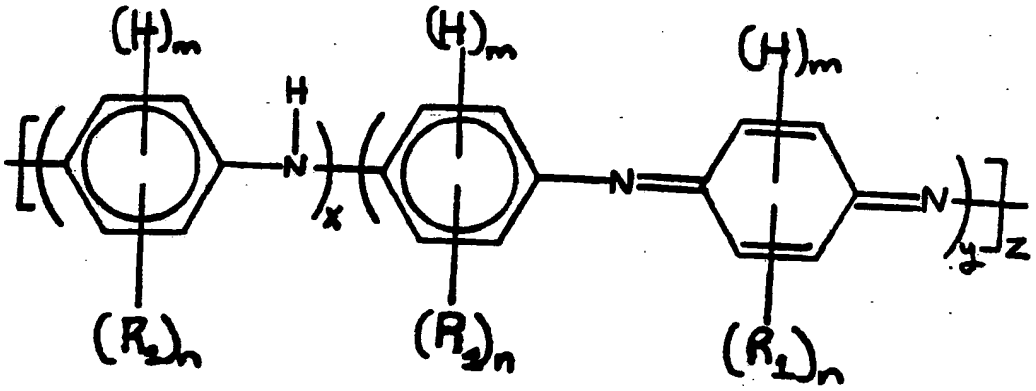


Formula III



or a combination thereof having various ratios of the above repeat units in the polyaniline backbone such as leucoemeraldine, protoemeraldine, emeraldine, nigraniline and pernigraniline. Polyanilines in the practice of this invention are more preferably those of the Formula IV:

Formula IV



wherein:

m, m, and R_1 and R_2 are as described above;

x and y are the same or different at each occurrence and are integers equal to or greater than 0, with the proviso that the sum of x and y is greater than 0, preferably where x is an integer equal to or greater than 0 and/or that the ratio of x to y is greater than or equal to about 0, more preferably said rati is equal to or greater than 0.5 and most preferably said ratio is equal to or greater than about 1; and

z is the same r different at each occurrenc and is

an integer equal to or greater than about 5.

Preferred for use in the practice of this invention are polyanilines of the above Formula IV in which:

n is an integer from 0 to about 2;

m is an integer from 2 to 4, with the proviso that the sum of n and m is equal to 5;

R_1 is alkyl, alkoxy or sulfonic acid or a salt or ester derivative thereof;

R_2 is hydrogen or methyl;

x is an integer equal to or greater than 1;

y is equal to or greater than 0,

with the proviso that the ratio of x to y is greater than about 1; and

z is an integer equal to or greater than about 5;

Particularly preferred for use in the practice of this invention are polyanilines of the above Formula IV in which:

n is an integer from 0 to 1;

m is an integer from 3 to 4, with the proviso that the sum of n and m is equal to 4;

R_1 is alkyl or alkoxy having from 1 to about 20 carbon atoms;

R_2 is hydrogen;

x is an integer equal to or greater than 2;

y is equal to or greater than 0, with the proviso that the ratio of x to y is greater than about 2; and

z is an integer equal to or greater than about 5.

Amongst the particularly preferred embodiments, most preferred for use in the practice of this invention are polyanilines of the above Formula IV in which:

n is an integer from 0 to 1;

m is an integer from 3 to 4, with the proviso that the sum of n and m is equal to 4;

R_1 is alkyl or alkoxy from 1 to about 6 carbon atoms (preferably from 1 to about 3 carbon atoms);

R_2 is hydrogen;

x is an integer equal to or greater than 2;

y is equal to or gr ater than 1, with the proviso that th rati f x t y is great r than ab ut 2; and

z is an integer equal to or greater than about 5.

In the embodiments of this invention of choice, the polyaniline is derived from unsubstituted aniline.

In general, the number of repeat units in the polyaniline homopolymer or copolymer are not critical and may vary widely. The greater the number of repeat units the greater the viscosity and molecular weight of the polyaniline homopolymer or copolymer. In those applications where a polyaniline homopolymers or copolymers of relatively low molecular weight and viscosity is required, such materials may be used, and in those applications where a polyaniline hompolymer or copolymer of relatively high molecular weight and viscosity is required, then such materials can be used. The number of repeat units is at least about 10. The upper limit can vary widely depending on the desired molecular weight and viscosity and the required degree of processibility, such as melt processibility, solution processibility and the like. In the preferred embodiments of the invention, the number of repeat units is at least about 20, and in the particularly preferred embodiments, the number of repeat units is at least about 30. Amongst the particularly preferred embodiments, most preferred are those embodiments in which the number of repeat units is at least about 40.

Polyaniline homopolymers and copolymers can be conveniently prepared throught conventional procedures. Such procedures are well known in the art and will not be described herein in great detail. See for example U.S. Patent Nos. 4,940,640; 4,711,742; 4,521,589; 4,855,361; 4,798,685; 4,806,271; 4,822,638; 4,851,487; 4,940,517; 4,808,681; 4,983,322; 5,006,278 and 4,900,782 and "The Handbook f Conducting P lymers", edited by Terje A. Skotheim, Marcell Dikker, Inc. New Y rk and Basel and references cited th rein, all f which is hereby

incorporated by reference. For example, preferred polyanilines can be prepared through use of chemical and electrochemical synthetic procedures. For example, one form of polyaniline can be prepared chemically by treating aniline with a suitable oxidant such as ammonium persulfate, $(NH_4)_2S_2O_8$, in excess acid such as 1M HCl and can be prepared electrochemically by the oxidation of aniline in aqueous fluoroboric acid electrolyte on a platinum foil anode.

The polyaniline homopolymer or copolymer is doped with a suitable phosphorus acid dopant to render the polymer electrically conductive, i.e. an electrical conductivity of at least about 10^{-8} ohm $^{-1}$ cm^{-1} by the four-in-line probe method. Any doping procedure may be used. Such methods are conventional and will not be described herein in any great detail. For example, the polyaniline homopolymer or copolymer is best doped by contacting the dopant with the polymer for a time sufficient to dope the polymer to the desired extent. The polymer can be contacted with the dopant in the gaseous state, in the liquid state, neat, or diluted by some suitable dilutent such as a gas as for example air, or liquid such as water, or an organic liquid. The dopant can be contacted with the polyaniline homopolymer or copolymer either during polymerization or after polymerization. In a preferred embodiment of the invention, the polyaniline homopolymer or copolymer may be doped in either by carrying out the polymerization in the presence of an acid having a pKa in the solution equal to or less than that of the homopolymer or copolymer. In general, the higher the pKa of the polyaniline homopolymer or copolymer, the higher the acid pKa can be used to provide a conductive polymer; and conversely, the lower the pKa of the polyaniline polymer the lower the pKa of the acid can be used to provide a desired degree of electrical conductivity. The pKa of the acid is preferably equal to or less than about 5,

more preferably equal to or less than about 4, and the most preferably equal to or less than about 3.

In another preferred embodiment of the invention, the polyaniline copolymer or homopolymer can be doped after polymerization. For example, the polyaniline homopolymer or copolymer layer is doped by contact with a solution of the dopant in a suitable solvent such as water.

As a second essential ingredient, the polyaniline of this invention is doped with a "thermally stable phosphorus acid dopant". As used herein, a "thermally stable phosphorus acid dopant" is a phosphorus acid which the is capable of doping the polyaniline to an electrical conductivity of at least about 10^{-8} ohm $^{-1}$ cm^{-1} by the four-in-line probe method and which retains at least about 10% of the dopant on heating the doped polyaniline at a temperature of 150°C for a period of 10 min. under dynamic vacuum. In general, the acid has a pKa equal to or less than that of the substituted or unsubstituted polyaniline under use conditions. In general, the higher the pKa of the substituted or unsubstituted polyaniline the higher the acid pKa that can be used to provide a conductive polymer; and conversely, the lower the pKa of the substituted or unsubstituted polyaniline, the lower the pKa of the acid necessary to provide a desired degree of electrical conductivity. The pKa of the acid is preferably equal to or less than about 5, more preferably equal to or less than about 4, and the most preferably equal to or less than about 3.

Preferred dopants are those containing anionic moieties of the formula:

$$R_4(PO_3^-)_x(PO_2(R_5)^-)_z(PO_2^-)_x(PO(R_5)^-)_x$$

and having one or more cationic moieties selected from the group consisting of:

$$M^{+z}$$

wherein:

R_4 is the same or different at each occurrence and

is an organic radical which may optionally include one or more heteroatoms such as phosphorus, nitrogen, oxygen, sulfur or the like;

R_6 is the same or different at each occurrence and is hydrogen or is selected from among R_4 substituents;

M is a species having a positive charge equal to s, provided that at least one of M^{+s} is a proton or a moiety which can be transformed by suitable means such as radiation, heat, chemicals and the like, into a proton under use or process conditions such as NH_4^+, $^+N(CH_3)_2H_2$, $^+N(C_2H_5)H_3$, Ph_3S^+, and the like;

s is an integer equal to or greater than 1;

r is the same or different at each occurrence and is 0 or an integer equal to or greater than 1, with the proviso that at least one of r is other than 0.

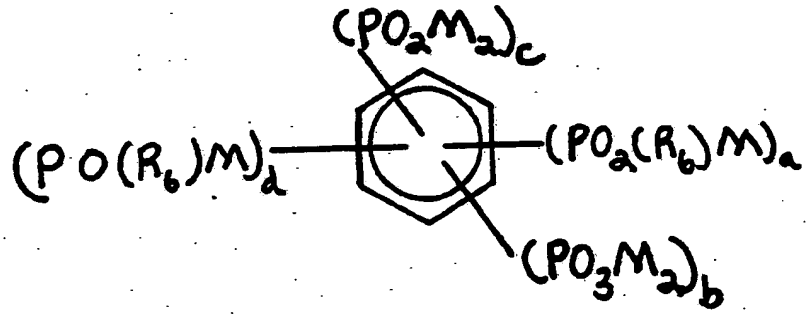
More preferred dopants are of the formula:

$$R_4(PO_2(R_6)M)_a(PO_3M_2)_b(PO_2M_2)_c(PO(R_6)M)_d$$

or

$$A-[-[-(X_1)_z-(R_7)_g-(X_2)_h-(R_8)_i-]_j-(B)_j-]_k-C$$

or



wherein:

M is H^+, or other metal or non-metal cation with the proviso that at least one of M is H^+ or a moiety which can be transformed into a proton under use or process conditions by suitable means such thermal, chemical or

ph t chemical m ans, as f r exampl , $^{+}NH_4$, $^{+}N(CH_3)_2H_2$, Ph_3S^{+}, $^{+}N(C_2H_5)H_3$ and the like

a, b, c, d and e are the same or different and are 0 or integers equal to or greater than 1, with the proviso that at least one of a, b, c or d is other than 0;

f, g, h, i and j are the same or different at each occurrence and are 0 or 1;

k is 0 or an integer equal to or greater than 1;

i is 0 or an integer equal to or greater than 1;

R_6 is hydrogen, substituted or unsubstituted alkyl, arylalkyl, alkylaryl, aryloxy, arylalkoxy, alkoxyaryl, alkoxyalkyl, or alkoxy wherein the permissible substitutent are selected from the group consisting of R_4 substituents;

R_4 is substituted or unsubstituted alkylamino, dialkylamino, arylamino, diarylamino, arylalkoxy, aryloxy, alkylarylamino, alkylsulfinyl, alkylsulfonyl, alkoxy, alkyl, arylalkyl or alkoxyalkyl, wherein permissible substituents are perhaloalkyl, phenyl, alkoxy, halo, cyano, amino, haloalkyl, hydroxy, sulfonic acid and salts and esters thereof, phosphoric acid and salts and esters thereof, boric acid and salts and esters thereof, sulfinic acid and salts and esters thereof, phosphinic acid and salts and esters thereof, phosphonic acid and salts and esters thereof, carboxylic acid and salts and esters thereof, nitro, and the like; or a polymeric radical of a polymeric acid, such as the polymeric radical of poly(vinyl phosphonic acid), poly(styrene phosphonic acid), poly(vinyl phosphinic acid), poly(styrene phosphinic acid), and the like;

$-X_1-$ and $-X_2-$ are the same or different at each occurrence and are $-O-$, $-N(R_6)-$, $-S-$, $-Se-$, $-OC(O)-$, $-N(A)-$, $-(O)CO-$, $-S(O)_2-$, $-OS(O)_2-$, $-SO(O)_2-$, or $-P(R_6)-$;

R_7 and R_8 are th same r different at each ccurr nc and is alkylen , arylene, or dialkylenearylene;

R_8 is hydrogen or is selected from the group of R_4 substituents;

A- is $-PO_3M_2$, $-PO_2(R_6)M$, $-PO_2M_2$ or $-PO(R_6)M$

-B- is $-PO_2M-$, $-POM-$ or $-PO(R_6)-$;

C- is OM;

R_5 is the same or different at each occurrence and is selected from the group consisting of amino, hydroxy, or substituted or unsubstituted R_4 substituents, aryl, amino, hydroxy or any two R_5 substituents together may form an unsubstituted or substituted alkylene or alkenylene chain completing a ring system which chain may optionally contain one or more divalent heteroatoms such as -O-, -S-, $-S(O_2)-$, -N(H)- and the like, wherein permissible substituents are one or more halo, phosphoric acid and salts and esters thereof, hydroxy, boric acid and salts and esters thereof, nitro, cyano, amino, phosphinic acid and salts and esters thereof, alkylamino, dialkylamino, alkylthio, alkoxyalkyl, alkylsulfinyl, alkylsulfonyl, alkoxy, alkylarylamino, arylamino, diarylamino, sulfinic acid and salts and esters thereof, phosphonic acid and salts and esters thereof, sulfonic acid and salts and esters thereof or carboxylic acid and salts and esters thereof, or R_4, R_5 or R_8 is a moiety of the formula:

$$-(OCH_2CH_2)_qOCH_3 \text{ or } -(OCH_2CH(CH_3))_qOCH_3$$

wherein:

q is a positive whole number from 1 to about 10.

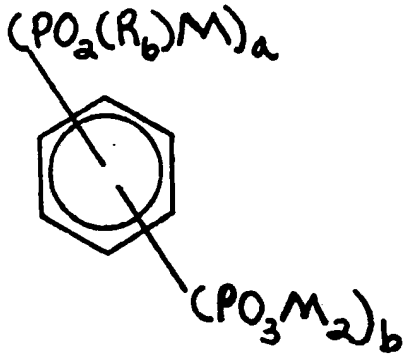
More preferred dopants are acids and/or acid derivatives of the formula:

$$R_4(PO_2(R_6)M)_a(PO_3M_2)_b$$

or

$$A-[-[-(X_1)_f-(R_7)_g-(X_2)_h-(R_8)_i-]_j-(B)_j-]_k-C$$

or



wherein:

a, b and e are the same or different and are 0, 1 or 2, with the proviso that at least one of a or b is not 0;

f, g, h, j and l are the same or different and are 0 or 1;

k is 0 or an integer from 1 to about 400;

i is 0 or an integer from 1 to about 20;

R_4 is alkyl, alkoxy, phenylalkoxy, alkoxyalkyl or phenylalkyl, either unsubstituted or substituted with one or more hydroxy, amino, fluoro, sulfonic acid or salts or esters thereof, or phosphoric acid or salts or esters thereof;

$-X_1-$ and $-X_2-$ are the same or different at each occurrence and are $-O-$, $-N(R_8)-$ or $-N(A)-$;

A- is $-PO_3M_2$ or $-PO_2(R_8)M$;

-B- is $-POM-$, $-PO_2M-$ or $-PO(R_8)-$;

C- is $-OM$;

R_5 is the same or different at each occurrence and is selected from the group consisting of halo, hydroxy, amino, alkylamino or dialkylamino, or substituted or unsubstituted alkyl, alkoxy, alkoxyalkyl, phenyl, alkylamino or dialkylamino, wherein permissible substituents are one or more phenyl, hydroxy, amino, sulfonic acid r salts r st rs there f, phosphori acid r a salt or ester ther of, or phosph nic acid or a salt or ester there f, r phosphonic acid or a salt or est r ther f r any tw R_5 substituents together may form an

alkenyl n chain completing a naphthalen , anthracene or phenanthrene fused system that may ptionally contain heteroatoms, and which may optionally be substituted with one or more alkyl, alkoxy, fluoro, perfluoroalkyl, amino, hydroxy, phosphonic acid or a salt or ester thereof, phosphoinic acid or a salt or ester thereof, fluoroalkyl, sulfonic acid or salts or esters thereof;

M is H^+ or other metal or non-metal cation, with the proviso that at least one of M is H^+ or is a moiety which can be thermally transformed into a proton under process conditions;

R_6 and R_8 are the same or different at each occurrence and are hydrogen, alkyl, alkoxy, phenoxy or phenyl either unsubstituted or substituted with one or more alkyl or alkoxy groups; and

$-R_7-$ and $-R_9-$ are the same or different and are alkylene, phenylene or dialkylenephenylene.

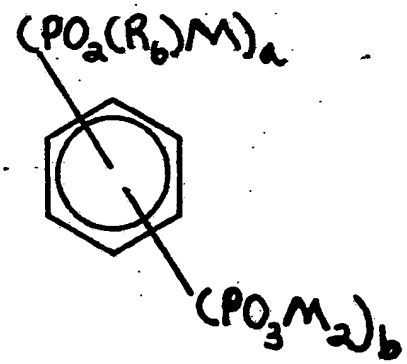
In the especially preferred embodiments of this invention, useful dopants are acids or acid derivatives of the formula:

$$R_4(PO_2(R_6)M)_a(PO_3M_2)_b$$

or

$$A-[-[-(X_1)_z-(R_7)_g-(X_2)_h-(R_8)_i-]_i-(B)_j-]_k-C$$

or



wherein:

a and b are the same or different and are 0,

1, 2 r 3, with the provis that at least on f a and b is n t 0;

e is 0, 1 or 2;

f, g, h, j and l are the same or different and are 0 or 1;

k is an integer from 1 to about 200;

i is an integer from 1 to about 10;

R_4 is alkyl, alkoxy or phenylene either unsbstituted or substituted with one or more fluoro groups;

R_5 is the same or different at each occurrence and are substituted or unsubstituted alkyl or alkoxy wherein permissible substituents are one or more fluoro, or any two R_5 substituents together may form an alkylene or alkenylene chain completing a naphthalene, anthracene or phenanthrene fused system, that optionally contains heteroatoms, which may be substituted with one or more alkyl, perfluoroalkyl, alkoxy, hydroxy, amino, or sulfonic acid or a salt or an ester thereof;

R_6 is hydrogen, alkoxy, alkyl, or phenoxy or phenyl either unsubstituted or substituted with one or more alkyl or alkoxy groups;

R_8 is hydrogen, alkyl or phenyl;

$-R_7-$ and $-R_9-$ are the same or different and are alkylene;

$-X_1-$ and $-X_2-$ are the same or different and are $-O-$, $-N(R_8)-$ or $-N(A)-$;

C- is -OM;

A- is $-PO_3M_2$ or $-PO_2(R_6)M$;

-B- is $-POM-$, $-PO_2M-$ or $-PO(R_6)-$; and

M is H^+ or other metal or non-metal cation or a moiety which can be thermally tranformed into a proton under process conditions with the proviso that at least one M is H^+.

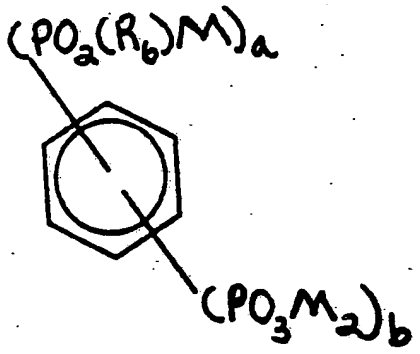
In th pr cess of th embodiment f this invention of choice, the dopant is an organic phosphorous acid or acid derivative f the formula:

$$R_4(PO_2(R_6)M)_a(PO_3M_2)_b$$

or

$$A-[-[-(X_1)_f-(R_7)_g-(X_2)_h-(R_8)_i-]_l-(B)_j-]_k-C$$

or



wherein;

a and b are the same or different and are 0, 1, 2 or 3 with the proviso that at least one of a or b is not zero(at least one of a or b is preferably 1);

g is 0 or 1 (preferably 1);

e is 0, 1 or 2 (preferably 0 or 1, more preferably 1);

f, h and l are the same or different and are are 0 or 1 (preferably 0);

j is 0 or 1 (preferably 1);

k is 0 or an integer from 1 to about 100 (preferably from 1 to about 10);

i is 0 or an integer from 1 to about 8 (preferably 1 to about 4);

R_4 is alkyl or alkoxy (preferably of from 1 to about 10 carbon atoms, more preferably of from 1 to about 6 carbon atoms and most preferably from 1 to about 3 carbon atoms);

R_7 and R_8 are alkylene (preferably of from 1 to about 40 carbon atoms, more pr ferably f from 1 to about 20 carbon atoms and most pr ferably of from 1 to about 10 carbon atoms)

R_5 is th same r different at each ccurrenc and

is hydroxy, alkyl or alkyl substituted with one or more fluoro groups, or two R_5 groups together may form an alkenylene chain completing a naphthalene fused ring system which may be substituted with one or more hydroxy, alkyl or perfluoroalkyl;

R_6 and R_8 are the same or different and are hydrogen or alkyl (preferably of from 1 to about 7 carbon atoms);

$-X_1-$ and $-X_2-$ are the same or different and are $-O-$, $-N(R_6)-$ or $-N(A)-$;

C- is $-OM$;

A- is $-PO_3M_2$ or $-PO_2(R_6)M$;

-B- is $-POM-$, $-PO_2M-$ or $-PO(R_6)-$; and

M is a proton, or other metal or non-metal cation, with the proviso that at least one of M is proton.

The amount of dopant included in the polyaniline is not critical and may vary widely. In general, sufficient dopant is included such that the polyaniline is doped to the desired extent, usually an amount such that the polyaniline is doped to a conductivity of at least about 10^{-8} $ohm^{-1}cm^{-1}$. The amount of dopant employed is preferably sufficient to provide a conductivity of at least about $10^{-8}ohm^{-1}cm^{-1}$, more preferably at least about $10^{-3}ohm^{-1}cm^{-1}$ and most preferably at least about $10^{-1}ohm^{-1}cm^{-1}$.

The doped polyaniline of this invention has many uses such as the formation of coatings, inks, films, articles and the like. The polyaniline of this invention is especially useful in the formation of the composition of this invention. Such composition comprises one or more of the polyanilines of this invention and one or more other organic or inorganic materials such as polymers, inorganic fillers and the like. In the preferred embodiments of the invention, the composition comprises one or more of the polyanilines in a matrix comprising one or more other electrically conductive or electrically non-conductive homopolymers or copolymers. The type of homopolymer or copolymer employed to form the

p lymer matrix may vary wid ly and any type can be used. Illustrative of useful p lymers are el ctrically conductive and/or non-conductive thermoplastic and/or thermosetting polymers. Thermoset polymers for use in the practice of this invention may vary widely. Illustrative of such useful thermoset polymers are alkyds derived from the esterification of a polybasic acid such as phthalic acid and a polyhydric alcohol such as glycol; allylics such as those produced by polymerization of dialkyl phthalate, dialkyl isophthalate, dialkyl maleate, and dialkyl chlorendate; amino resins such as those produced by addition reaction between formaldehyde and such compounds as melamine, urea, aniline, ethylene urea, sulfonamide and dicyandiamide; epoxies such as epoxy phenol novolak resins, diglycidyl ethers of bisphenol A and cycloaliphatic epoxies; phenolics such as resins derived from reaction of substituted and unsubstituted phenols such as cresol and phenol with an aldehyde such as formaldehyde and acetaldehyde; polyesters; silicones; and urethanes formed by reaction of a polyisocyanate such as 2,6-tolylene diisocyanate, 4,4-diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate and 4,4'-dicyclohexylmethane diisocyanate with a polyol such as polyether polyol (trimethylol propane, 1,2,6-hexanetriol, 2-methyl glycoside, pentaerythitol, poly(1,4-tetramethylene ether) glycol, sorbitol and sucrose); polyester polyols such as those prepared by esterification of adipic acid, phthalic acid and like carboxylic acids with an excess of difunctional alcohols such as ethylene glycol, diethylene glycol, propanediols and butanediols.

Thermoplastic polymers for use in the practice of this invention may vary widely. Illustrative of such thermoplastic polymers are polyesters such as p ly(1,2-dimethylpr piolacton), p ly(pivaloyl lactone), p ly(para-hydroxybenz ate), p ly(ethylene xybenzoate), poly(ethylene terephthalate), poly(1,4-cycl hexane

dimethylen terephthalate), and th lik ; p lyamides such as p ly(4-amin butyri acid) (nyl n 4), poly(6-amino-hexanoic acid) (nylon 6), poly(11-aminoundecanoic acid) (nylon 11), poly(12-aminododecanoic acid) (nylon 12), poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide), (nylon 6,10), poly(meta phenylene isophthalamide) (Nomex), poly(p-phenylene terephthalamide) (Kevlar), and the like; polycarbonates such as poly[methane bis(4-phenyl)carbonate], poly[1,1-ethane bis(4-phenyl)carbonate], and the like; polymers derived from the polymerization of α,β-unsaturated monomers such as polyethylene, acrylonitrile/butadiene/styrene terpolymer, polypropylene, poly(4-methyl-1-pentene), polyisobutylene, poly(isoprene), poly(vinyl fluoride), poly(vinyl chloride), poly(vinylidene fluoride), poly(vinylidene chloride), poly(tetrafluoroethylene) (Teflon), poly(chlorotri-fluoroethylene), poly(methyl acrylate), poly(methyl methacrylate), poly- acrylonitrile, polyacrylamide, and the like; polydienes such as poly(1,3-butadiene) (cis), poly(1,3-butadiene) (trans), poly(1,3-butadiene)(mixt.), and the like; polyoxides such as poly[2,2-bis(chloromethyl)-trimethylene-3-oxide] (penton), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(2,6-diphenyl-1,4-phenylene oxide) (Texax, P30), and the like; polysulphides such as poly(phenylene sulphide) and the like; polysulfones such as poly[4,4'-isopropylidene diphenoxy di(4-phenylene) sulphone]; noryl; and mixtures thereof. Preferred polymers are polymers formed from 1,2 unsaturated monomers such as polyolefins and polyvinyls, and other thermoplastic polymers such as polyesters, polyamides and polycarbonates.

The composition f this inventi n may include various optional components such as plasticizers,

blending aids, c l rants, flam -retardants and the like, or components which either fill or from a substrat for the composition to be cast from the melt or solution. These other components may vary widely and may include any material known for use in conventional polymer compositions. Illustrative of such other components are such materials as carbons, metal conductors, reinforcing fibers, inert fillers, glass beads, clays, other conductive and non-conductive polymers, conductive ceramics, super-conductive ceramics, and the like.

The composition of this invention can be prepared using conventional techniques as for example conventional melt or solution blending techniques. For example, such compositions can be formed by heating and mixing a mixture of the various components to a temperature which is equal to or greater than the melting point of flow point of at least one of the polymer components to form a molten intimate mixture to which optional components may be added as desired. Thereafter the mixture can be formed into a desired article through use of any conventional shape forming technique. For example, the molten mixture can be spread on a surface and allowed to cool forming free standing films or coatings. The molten mixture can be extruded through a die to form films or fibers, or injection molded into a suitable mold to form molded parts having the shape of the mold. The manner in which the molten mixture is formed is not critical and conventional methods can be employed. For example, the molten mixture can be formed through use of conventional polymer and additive blending means, in which the polymeric components are heated to a temperature equal to or greater than the melting point of at least one of the polymers, and below the degradation temperature of each of the polymers. Ultrasonication can be used to improv dispersion f the non-s lubl phas s. The desired amount of the optional ingredients in a liquid or powder d form is added t th melted p lymers while at the same tim

vig r sly agitating th m lt as f r example by stirring r irradiating with ultrasound, r add d pri r t m lting and mixing.

In a solution process for the preparation of the composition of this invention, a solution is formed of the desired host polymer and a desired polyaniline of this invention in a suitable solvent with or without a dopant solute. As used herein, "solutions" are pure solutions or dispersions of particles in which particle size is equal to or less than about 500 nanometers, preferably less than about 300 nanometers more preferably less than about 200 nanometers and most preferably less than about 100 nanometers. The desired optional components in the desired amounts may be dissolved or dispersed in the solution. The dissolved and/or dispersed polymers can be solidified into a desired shape by removal of the solvent through use of conventional techniques. For example, by removal of the solvent from a solution spread on a surface films can be formed of any desired thickness. By extruding the solution through a die, fibers and films can be made. Similarly, by removing the solvent from the solution in a mold, shaped articles conforming in shape to the mold can be prepard. If the original solution did not include a suitable dopant, the shaped article can be exposed to a suitable dopant to dope the polyaniline. In the preferred embodiments of the invention, however, doped polyaniline is used to form the solution.

In the most preferred embodiment of the invention, the components of the intimate mixture can be granulated, and the granulated components mixed dry in a suitable mixer, as for example using ultrasonication or a tumbler or a Branbury Mixer, or the like, as uniformly as possibl . Thereafter, th composition is heat d and further mixed in an extruder when at least ne f th polymers components is melted. As described above, th fluid mixture is thereafter ejected with co ling.

The order of mixing of the various components of the intimate mixture may not be critical. Accordingly, the order of addition of the polymers and other optional components to be described in more detail hereinbelow, to form the initimate mixture, can be varied as desired.

The electrically conductive polyaniline of the invention, and the composition of this invention can be used for any purpose for which conductive polymers are useful. Examples of articles include conductive polymer housings for EMI Shielding of sensitive electronic equipment such as microprocessors; infrared, radio frequency and microwave absorbing shields; flexible electrical conducting connectors; conductive bearings and brushes; semiconducting photoconductor junctions; electrodes; capacitors; optically transparent or non-transparent corrosion-preventing coatings for corrodible materials such as steel; antistatic materials and optically transparent or non-transparent coatings for packaging electronic components; carpet fibers; waxes for floors in computer rooms; antistatic finishes for CRT screens, aircraft, and auto windows; and the like.

Various other applications are anticipated for the conducting coatings produced by the present processes, such as in conducting plastic gas tanks; solar window coatings; transparent electrical elements for heated windows and heated liquid crystal displays; electrochromic displays, electrical contacts for electroluminescent displays and electroluminescent lights, and electrical contacts for piezoelectric films for transparent loud speakers; transparent conducting coatings for windows in burglar alarm systems; membrane coatings for chemical separations (such as O_2 and N_2, for example); and conducting coatings for membrane switches; and a discharg layer r photor sist layer for lithographic process.

Specially us ful c atings f c nducting polymers are those which ar transparent in the visible sp ctral

regi n. By transparent in the visibl r gion, it is meant that at least 30% of the solar en rgy spectrum in the visible region is transmitted by the coating. Since transparency is inversely related to conducting polymer thickness, a desired degree of transparency can be obtained by limiting the thickness of this layer, such as by limiting the amount of conductive polymer solution applied onto the surface of the substrates.

The following specific examples are presented to more particularly illustrate the invention, and should not be construed as being limitations on the scope of the invention.

EXAMPLE 1

To a solution containing 1770 mL of H_2O, 50 g of aniline(0.54 mole) and 172 g p-toluene sulfonic acid (0.90 mole) was added, dropwise at 15°C, a solution of ammonium persulfate (153.4 g in 336.5 mL H_2O) over a period of 40 minutes. After addition, the reaction was allowed to continue at 15°C for a 0.5 hours.

The resultant solid precipitate was collected and washed with 6 L of an aqueous toluene sulfonic acid solution (10 wt%) and then by 3 L of methanol. The resultant blue-black solid was dried in air for 25 hrs and dried at 130°C for 3 hrs. under dynamic vacuum to give poly(anilinium tosylate) as a green powder. The conductivity of the dried and pressed pellet formed from this material was 1 S cm^{-1} as measured by the co-linear four-probe method. The conductivity of the moisture-saturated pellet was 20 S cm^{-1}.

The yield was 78g. The intrinsic viscosity (in concentrated H_2SO_4, at 25°C) was 0.66 dL/g. Elemental analysis of the dried green powder gave:

C:64.27(Wt%)	H:4.86%	N:8.59%
S:8.40%	O:13.51%	

Moisture: less than 0.8 wt%

EXAMPLE 2

Poly(anilinium tosylat) (13g) obtained from Example 1 was suspended in water at room temperature and nuetralized with excess sodium carbonate (Na_2CO_3). The suspension was then filtered and the cake was dried to yield a blue-black powder of polyaniline base.

EXAMPLES 3 TO 6 AND COMPARATIVE EXAMPLES 1 AND 2

The neutral polyaniline obtained in Example 2 was then redoped with various different phosphorous-containing dopants by the following procedure.

The neutral polyaniline (2 g) was suspended in 25 mL methanol containing 5 g of the corresponding phosphorous-containing acids and perfluorocarboxylic acids as listed in Table 1. The resulting solution was stirred for 20 hours. The solid was then collected and rinsed with 50 mL of methanol. after air-drying for overnight, the doped polyaniline was dried at 80 C under dynamic vacuum for 3 hours.

The conductivities, listed in Table 1, were measured by a 4-in-line probe on a pressed pellet of about 1 cm diameter. The TGA (thermogravimetric analysis) of these doped polyanilines were performed by DuPont 9900 Thermal Analysis at a heating rate of 20° C/min from 25°C to 900°C under an inert gas. The on-set temperatures corresponding to the loss of the dopant species of each doped polyanilines are summaried in Table 1. The results showed that all these phosphorous-containing dopant are thermally much more stable then carboxylic acids.

TABLE 1

EX. NO.	DOPANT	CONDUCTIVITY S/cm	ON-SET TEMPERATURE OF LOSING DOPANT
COMP EX	Perfluorooctanoic acid	0.003	125
COMP EX 2	Perfluorodecanoic acid	0.002	140
EX 3	Nitrilotris(methylene) triphosphonic acid	13.2	260
EX 4	Phenylphosphonic acid	0.22	290
EX 5	Methylenediphosphonic acid	0.41	275
EX 6	Phenylphosphinic acid	2.67	240

*a. Results based on TGA (thermogravimetric analysis)

EXAMPLE 7 AND COMPARATIVE EXAMPLE 3

The polyaniline doped with methylenediphosphonic acid prepared in Examples 3 to 6 and comparative Examples 1 and 2 and the one doped with p-toluene sulfonic acid prepared in Example 1 were subjected to thermal stability study. The study was done by heating a pellet of the above two polyaniline compositions in a glass chamber under dynamic vacuum at 270 C° for 30 minutes. The conductivities of the pellet before and after heating were measured by a 4-in-line probe. The results, as summarized in the following tables, indicated that the thermal stability of the phosphonic acid doped polyaniline is much higher than that of the sulfonic acid doped polyaniline.

TABLE 2

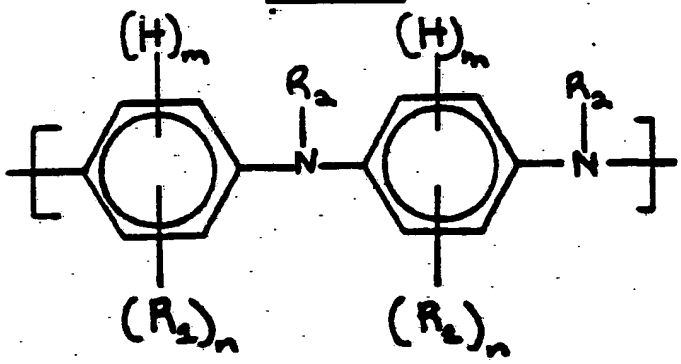
EX.NO	Dopant	Conductivity(S/cm)	
		at 25°C	at 270 C, 30 min.
COMP EX 3	p-Toluenesulfonic acid	1.8	$<1 \times 10^{-10}$
EX 7	Methylene phosphonic acid	0.4	4×10^{-9}

WHAT IS CLAIMED IS:

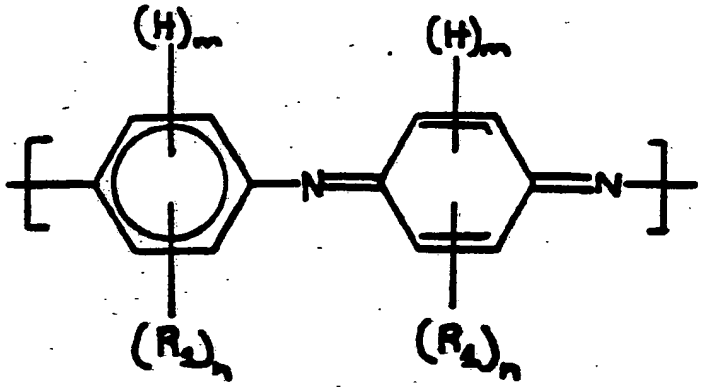
1. A thermally stable electrically conductive polyaniline comprising a polyaniline homopolymer or copolymer doped with an organic phosphorus acid.

2. A polyaniline according to claim 1 wherein the polyaniline comprises repeat units of the Formulas II, III or II and III:

Formula II



Formula III



wherein:

n is an integer from 0 to 4;

m is an integer from 0 to 4, with the proviso that the sum of n and m is 5;

R_1 is phosphinic acid or a salt or ester thereof, phosphonic acid or a salt or ester thereof, sulfonic acid or a salt or ester thereof, boric acid or a salt or ester thereof, phosphoric acid or a salt or ester thereof, alkylamino, dialkylamino, arylamino, diarylamino,

alkylarylamino, amino, hydroxy, sulfinic acid or a salt or ester thereof, nitro, carboxylic acid or a salt or ester thereof, halo, cyano, deuterium, or substituted or unsubstituted alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkynyl, dialkylamino, arylamino, diarylamino, alkylarylamino, aryloxy, hydroxy, alkylthioalkyl, alkylaryl, arylalkyl, aryloxy, amino, alkylthioalkyl, alkylaryl, arylalkyl, alkylsufinyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio, arylsulfinyl, alkoxycarbonyl, alkylsilane, or arylsulfonyl, wherein permissible substituents are one or more amino, alkylamino, dialkylamino, arylamino, diarylamino, phosphinic acid or a salt or ester thereof, alkylarylamino, phosphonic acid or a salt or ester thereof, sulfonic acid or a salt or ester thereof, boric acid or a salt or ester thereof, sulfinic acid or a salt or ester thereof, phosphoric acid or a salt or ester thereof, carboxylic acid or a salt or ester thereof, halo, nitro, hydroxy, cyano or epoxy moieties; or any two R_1 substituents, or any one R_1 substituent and R_2 substituent taken together may form substituted or unsubstitued alkylene, alkynylene or alkenylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic, heteroalicyclic, heteroaromatic or alicyclic carbon ring, which ring may optionally include one or more divalent ester, carbonyl, nitrogen, sulfur, sulfinyl, sulfonyl or oxygen, wherein permissible substituents are one or more amino, alkylamino, phosphinic acid or a salt or ester thereof, dialkylamino, arylamino, diarylamino, alkylarylamino, phosphonic acid or a salt or ester thereof, sulfonic acid or a salt or ester thereof, boric acid or a salt or ester thereof, sulfinic acid or a salt or ester thereof, phosphoric acid or a salt or ester thereof, carboxylic acid or a salt or ester thereof, halo, nitro, hydroxy, cyano or epoxy moieties, or R_1 is an aliphatic moiety having repeat units of the formula:

$(OCH_2CH_2)_qO\text{-}CH_3$, $(OCH_2CH(CH_3))_qO\text{-}CH_3$,

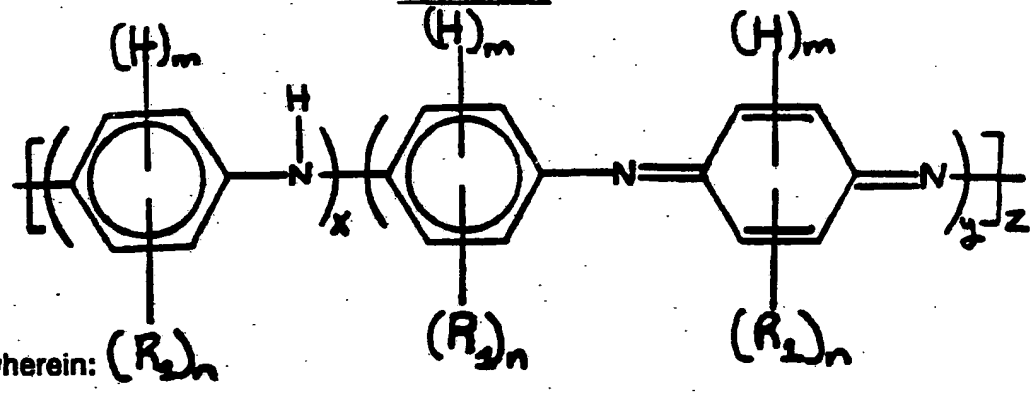
$(CH_2)_qCF_3$, $(CF_2)_qCF_3$ or $(CH_2)_q CH_3$

wherein q is a positive whole number; and

R_2 is the same or different at each occurrence and is hydrogen or substituted or unsubstituted alkyl group wherein permissible substituent is R_1.

3. A composition according to claim 2 wherein said homopolymer or copolymer is comprised of the Formula IV:

Formula IV



wherein:

x and y are the same or different at each occurrence and are integers equal to or greater than 0, with the proviso that the sum or x and y are greater than 0;

z is an integer equal to or greater than about 1;

n is an integer from 0 or 1;

m is an integer from 3 or 4, with the proviso that the sum of n and m is 4;

R_1 is the same or different at each occurrence and is alkyl or alkoxy having from 1 to about 12 carbon atoms or a sulfonic acid function or a salt or ester thereof; and

R_2 is the same of different at each occurrence and is alkyl or hydrogen

4. A composition according to claim 3 wherein R_2 is hydrogen.

5. A composition according to claim 3 wherein:

R_1 is the same or different at each occurrence and is alkyl or alkoxy having from 1 to about 6 carb n atoms;

x is an integer qual to or greater than 1;

R_2 is hydrogen;

y is equal t or greater than 0; and

z is an integer equal to r greater than ab ut 5.

6. A composition according to claim 10 wherein m is 4 and n is 0.

7. A composition according to claim 1 wherein said dopant is an organic phosphosphorus acid having a pKa less than that of said polyaniline.

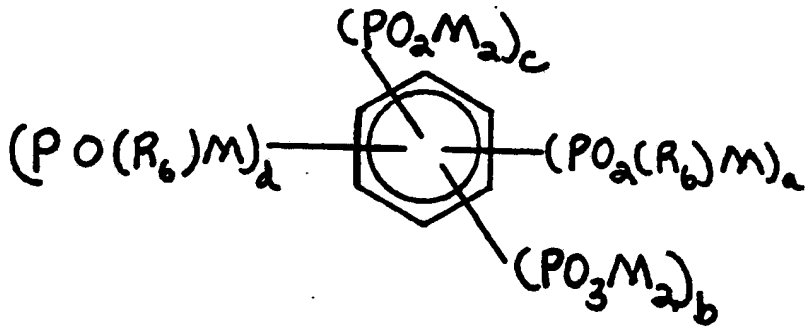
8. A composition according to claim 7 wherein said dopant is an acid or acid derivative of the formula:

$$R_a(PO_2(R_6)M)_d(PO_3M_2)_b(PO_2M_2)_c(PO(R_6)M)_d$$

or

$$A\text{-}[\text{-}[\text{-}(X_1)_f\text{-}(R_7)_g\text{-}(X_2)_h\text{-}(R_8)\text{-}]_i\text{-}(B)_j\text{-}]_k\text{-}C$$

or



wherein:

M is H^+, or other metal or non-metal cation with the proviso that at least one of M is H^+ or a moiety which can be thermally or chemically transformed into a proton under process or use conditions;

k is 0 or an integer from 1 to about 400;

i is 0 or an integer from 1 to about 20;

A is a moiety of the formula:

$$-PO_2(R_6)M \text{ or } -PO_3M_2 \text{ or } -PO_2M_2$$

B is the sam or different at each occurrence and is moieties f the formula: $-PO_2M-$, or -POM-, or $-POR_8-$

C is -OM

a, b, c and d are the same or different at each occurrence and are 0 or integers equal to or greater than 1 with the proviso that at least one of a, b, c or d is other than 0;

e is 0, 1, 2, 3 or 4; and

f, g, h, and j are the same or different at each occurrence and 0 or 1;

R_4, R_5 and R_6 are the same or different at each occurrence and are nitro, cyano, hydroxy, halo, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, alkoxy, or substituted or unsubstituted alkoxy, aryl or alkyl having from 1 to about 30 carbon atoms wherein permissible substituents include, perhaloalkyl, phenyl, alkoxy, halo, cyano, amino, haloalkyl, hydroxy, sulfonic acid or a salt or ester thereof, phosphoric acid or a salt or ester thereof, boric acid or a salt or ester thereof, sulfinic acid or a salt or ester thereof, phosphinic acid or a salt or ester thereof, phosphonic acid or a salt or ester thereof, carboxylic acid or a salt or ester thereof, nitro, or any two R_5, or any two R_6, or any R_4 and R_6 substituents together may form an alkenylene chain completing a fused-ring system which chain may be unsubstituted or substituted with one or more halo, phosphoric acid or a salt or ester thereof, hydroxy, boric acid or a salt or ester thereof, nitro, cyano, amino, phosphinic acid or a salt or ester thereof, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, sulfinic acid or a salt or ester thereof, phosphonic acid or a salt or ester thereof, sulfonic acid or a salt or ester thereof, or carboxylic acid or a salt or ester thereof, or R_4 or R_5 or R_6 is a moiety of the formula:

$$-(CH_2)_qCF_3,\ -(CF_2)_qCF_3,\ -(CH_2)_qCH_3$$

wherein:

q is a positive whole number from 1 to about 10;

$-(OCH_2CH_2)_qOCH_3$ or $-(OCH_2CH(CH_3))_qOCH_3$

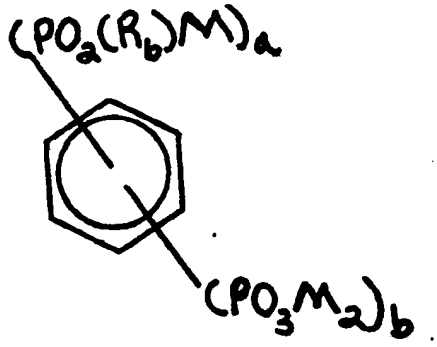
X_1 or X_2 are the same or different at each occurrence, and are the moieties of the formula: -O-, -S-, -OC(O)-, -(O)CO-, $-S(O)_2-$, -N(A)-, $-O-S(O)_2-$, $-(O)_2S-O-$, $-N(R_8)-$, $-P(R_8)-$

R_7 is substituted or unsubstituted alkylene, arylene or dialkylene arylene wherein the permissible substituent is R_1.

9. A composition according to claim 8 wherein said dopants are acids and/or acid derivatives of the formula:

$R_4(PO_2(R_6)M)_a(PO_3M_2)_b$

or



wherein:

a, and b are the same or different and are 0, 1 or 2 with the proviso that at least one of a or b is not 0;

A is moiety of the formula: $-PO_2(R_6)M$ or $-PO_3M_2$;

B is $-PO_2M-$ or -POM-, $-PO(R_6)-$

C is OM

e is 0, 1 or 2; f, g, h and; are the same or different and are 0 or 1;

f, g, h and j are th same or different and are 0 or 1;

k is an integer from 1 to about 200,

i is an integer from 1 to about 10,

R_4 and R_5 are the same or different at each occurrence and are alkyl, phenyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, or alkyl substituted with one or more fluoro, phosphonic acid or salt or ester thereof, sulfonic acid or a salt or ester thereof, alkoxy, hydroxy, nitro, cyano, phosphinic acid or a salt or ester thereof, amino, or carboxylic acid or a salt or ester thereof, or phenyl substituted with one or more alkyl, alkoxy, fluoroalkyl, phosphonic acid or a salt or ester thereof, sulfonic acid or a salt or ester thereof, phosphinic acid or a salt or ester thereof, hydroxy, nitro, cyano, or carboxylic acid or a salt or ester thereof, or any two R_5 substituents together may form an alkylene or alkenylene chain completing a naphthalene, anthracene or phenanthrene fused system which may be substituted with one or more alkyl, alkoxy, fluoro, phosphonic acid or a slat or ester thereof, phosphinic acid or a salt or ester thereof, fluoroalkyl, sulfonic acid or a salt or ester thereof, carboxylic acid or a salt or ester thereof hydroxy, nitro, amino or cyano groups;

R_6 is hydrogen, aryl, aryloxy, alkyl or alkoxy; and

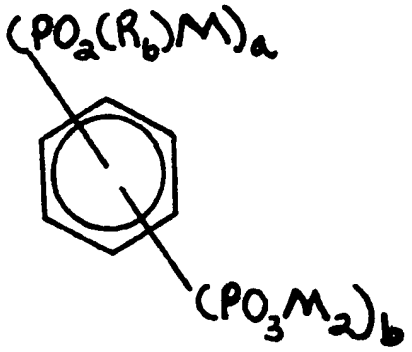
R_7 is alkylene, arylene or dialkylenearylene; and

M is H^+ or other metal or non-metal cation, with the proviso that at least one of M is H^+ or is a moiety which can be thermally transformed into a proton under process conditions.

10. A composition according to claim 9 wherein said dopant is a phosphorous acid of the formula:

$R_4(PO_3M_2)_b(PO_2(R_6)M)_a$

or



wherein;

c is 1, 2 or 3;

e is 0, 1 or 2;

R_4 is alkyl or alkoxy;

R_6 is hydrogen or alkyl;

R_5 is hydroxy, alkyl or alkyl substituted with one or more fluoro, or any two R_5 groups together may form an alkenylene chain completing a naphthalene fused system which may be substituted with one or more sulfonic acid or a salt or ester thereof, hydroxy, and

M is a proton, or other metal or non-metal cation, with the proviso that at least one of M is a proton.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/03960

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H01B1/12; C08G73/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	H01B ; C08G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[10]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
P,X	WO,A,9 305 519 (ALLIED-SIGNAL) 18 March 1993 see the whole document	1-6,8-10
P,X	WO,A,9 218 988 (ALLIED-SIGNAL) 29 October 1992 see the whole document	1-6,8-10
X,P	WO,A,9 215 632 (ALLIED-SIGNAL) 17 September 1992 see the whole document	1-6,8-10
P,X	WO,A,9 211 644 (ALLIED-SIGNAL) 9 July 1992 see the whole document	1-6,8-10
X	WO,A,9 010 297 (ALLIED-SIGNAL) 7 September 1990 see the whole document	1-6,8-10

* Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
30 JULY 1993	16. 08. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DROUOT M.C.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9303960
SA 73624

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 30/07/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9305519	18-03-93	None		
WO-A-9218988	29-10-92	None		
WO-A-9215632	17-09-92	US-A-	5171478	15-12-92
WO-A-9211644	09-07-92	None		
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		EP-A-	0461182	18-12-91
		JP-T-	3505892	19-12-91